



PATENT SPECIFICATION

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COMPLETE SPECIFICATION

A Process for dissolving Insoluble Collagen

We, NIHON HIKAKU KABUSHIKI KAISHA, a Japanese Body Corporate, of 1-1, Senjumidori-cho, Adachi-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for dissolving insoluble collagen.

In this specification and claims "insoluble collagen" means a collagen that cannot be usually dissolved in an aqueous alkaline or an inorganic salt solution.

Many processes for dissolving insoluble collagen in an aqueous solution in which collagen is dissolved in mono-molecular state have been proposed. The prior arts teach the methods of treating insoluble-collagen in aqueous acid solutions with various enzymes to obtain the collagen solution; that is, U.S. Patent Specifications No. 3,034,852 and 3,121,049 deal with the use of a proteolytic enzyme obtained from animal viscera, British Patent Specification No. 1,090,967 deals with the use of enzymes obtained from *Aspergilli* and British Patent Specification No. 1,119,342 employs enzymes produced from *Penicillium*. Further, U.S. Patent Specification No. 3,314,861 discloses dissolving insoluble collagen in an aqueous medium by the treatment with an enzyme having an optimum pH between 2 and 10 for milk casein in the presence of a cationic surfactant or a water soluble salt of divalent metal. In addition British Patent Specification No. 480,712 discloses the treatment of a natural gelatine forming material with a lime suspension containing a small proportion of a primary or secondary amine.

Collagens are classified into three kinds, according to solubility:

(1) neutral-salt-soluble collagen which is capable of being dissolved in an aqueous neutral-salt solution such as 0.5 M aqueous sodium chloride solution,

(2) acid-soluble collagen which is capable of being dissolved in an acid solution such as citrate buffer (citric acid plus sodium citrate) or dilute acetic acid solution, and

(3) insoluble collagen which cannot be dissolved in such solutions.

A collagen molecule is constructed with three polypeptide chains. These chains of neutral-salt-soluble collagen are substantially not cross-linked. By the time of biological maturation of soluble collagen two or three of these chains are cross-linked intramolecularly and covalently, as in the case of acid-soluble collagen. The molecules of these soluble collagens have specific parts, telopeptides, at the ends of the molecules. The structure of the telopeptides differs significantly from that of the backbone polypeptide chains. The telopeptides are relatively easily attacked by enzymes; the backbones stay intact. The insoluble collagen is further cross-linked. Thus, in the case of calf skin, two or more macromolecules are also inter-molecularly and covalently cross-linked at the telopeptides (thereby insolubilizing the soluble-collagen having only intramolecular cross-linking). With further biological aging (i.e. as the calf skin becomes steer hide) additional intra- and inter-molecular cross-linking takes place. The telopeptide portions in insoluble collagen are attacked by a proteolytic enzyme, and thereby solubilization of insoluble collagen can be carried out. However, the enzyme digestion of the telopeptide portions of the insoluble collagen of steer hide is very slow as compared with the analogous digestion of calf skin because of the additional cross-linking.

N. T. Crosby and G. Stainsby reported in Research 15 p.p. 427 (1962) that the insoluble collagen of calf skin is partially dissolved by treating it with 5% aqueous sodium hydroxide solution saturated with sodium sulfate at 20°C for five days. K. Kuhn, E. Zimmer, P. Waykole and P. Fietzak also

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reported in Z. Physiol. Chem. 333,209 (1963) that the insoluble collagen of calf skin is completely dissolved by the same process.

5 If the above-described process is applied to the insoluble collagen of steer hide (of adult animal), the yield of dissolved collagen is very low, due to the abundance of cross-links compared to calf skin.

10 It has been found that if the insoluble collagen of adult animal is treated with an aqueous alkali metal hydroxide and alkali metal sulfate solution containing a small amount of base selected from hydroxylamine, hydrazine and amines having from 1 to 15 5 carbon atoms, the action of alkali on the telopeptide portions is greatly accelerated and the insoluble collagen is converted into its soluble form. Then, upon treating with acid solution, the collagen is dissolved to obtain collagen solution.

20 In general, collagen swells in an aqueous caustic alkali solution. However, sodium sulfate present in the solution inhibits such swelling of collagen. Thus, lowering of the denaturation temperature of collagen due to alkali is prevented. Accordingly, the process according to this invention may be carried out at a relatively high temperature.

30 Any primary or secondary amine containing from 1 to 5 carbon atoms may be employed in this process. The amine may be any form, straight, branched or cyclic. Typical amines are monomethylamine, dimethylamine, ethylenediamine, piperidine 35 and piperazine. Other useful amines may be selected by anyone skilled in the art.

40 The concentration of base may be from 0.05 to 0.3 M. The concentration of alkali metal hydroxide such as sodium or potassium hydroxide may be from 0.3 to 1.0 N. The concentration of alkali metal sulfate such as sodium sulfate or potassium sulfate may be from 10% to 20% (w/v). The temperature of treatment is from 15° to 25°C 45 and the time is from five to fourteen days. In general, if the concentration of alkali metal sulfate is decreased or the concentration of alkali is increased, the temperature of treatment should be decreased.

50 The amine accelerates the hydrolysis due to alkali of only the telopeptide in the collagen; the backbone of the collagen is not hydrolyzed and retains its original structure. This differs from the prior art, for example 55 U.S. Patent Specification No. 2,184,494, in which collagen is treated with aqueous calcium hydroxide solution containing amine similar to those employed in this invention, since said combination hydrolyses not only 60 telopeptides but also the backbone of collagen thereby breaking it down into lower molecular weight material. Accordingly, an important feature of this invention is that the amine acts so as to ensure that only the 65 telopeptide portion and not the backbone

of the insoluble collagen is attacked by the alkali.

After the alkali treatment, the collagen fiber slurry is neutralized with any acid, 70 such as hydrochloric, sulfuric, acetic, citric or lactic acid. Then the slurry is thoroughly washed with water to remove the salt. The telopeptide portions in the collagen so treated are broken down and the fiber swells but there is no significant change in appearance. 75

Accordingly, the collagen fiber can be easily extracted with an acid solution to obtain collagen solution. Usable acids include hydrochloric, sulfuric, acetic, citric and lactic acids. The pH is adjusted to below 4.0. The amount of acid employed is adjusted so as to give a desired pH and concentration of collagen. The concentration of the resulting solution is usually about 8% by weight. 80

85 The collagen molecule in collagen solution obtained according to this invention is examined for intrinsic viscosity, flow birefringence, sedimentation by ultracentrifugal analysis and optical rotation and it has been determined that collagen molecules in the 90 solution are monomolecularly dissolved and retained their original structure. The solution can be extruded into regenerated collagen articles, such as fiber, film and tube by a conventional process. 95

A further important feature of this invention is that the collagen fiber, the collagen solution or the regenerated collagen fiber obtained according to this invention can be converted to gelatin by heating 100 the collagen solution or the collagen fiber in water at a temperature over the denaturation temperature of collagen. The resulting gelatin possesses an isoionic point of about 4.9 which is the same value as that of gelatin obtained by the liming process and it differs from the gelatin produced from the insoluble collagen by enzyme process only in respect to the isoionic point. 105

Commercial gelatins are usually manufactured by liming unhaird raw hide for a long time, for example, from 60 to 90 days, and by gelatinizing the limed hide in several extraction steps with warm water. The quality of the gelatins so obtained decreases 115 with each succeeding extraction stage. In contrast, according to this invention, a gelatin having high quality and uniform molecular weight can be produced by only a single extraction step after alkali-pretreatment of less than two weeks. 120

Example 1

Insoluble collagen fiber was obtained from hide as follows.

125 The butt of steer hide was unhaird and water-washed, then split to remove grain and flesh sides. The remaining intermediate layer (corium) which contains a larger amount of collagen than the others was washed with

water and soaked in 10% aqueous salt solution, then ground by a meat mill with cooling to obtain a slurry. In order to remove the neutral-salt-soluble and acid-soluble collagens which exist in a very small amount, the slurry was soaked in a 10% aqueous salt solution and in a 0.15 M citrate buffer for one to two days, then washed again with water. After adjusting the pH of the slurry to 7.0 by sodium hydroxide, the slurry was water-washed and the fiber was dehydrated with ethyl alcohol.

Then the collagen fiber was defatted with a mixture of ethyl alcohol and ethyl ether (1 : 1) and dried to obtain insoluble collagen fiber.

The fiber was treated as follows:

	collagen fiber	100	g
	NaOH	20	g
	Na ₂ SO ₄	160	g
	monomethylamine	6.21	g
	volume of the solution	1	l
	temperature of treatment	20	°C
	duration of treatment	2	weeks

During the treatment the collagen fiber was agitated for a short time a few times every day. Thereafter, the slurry was neutralized with hydrochloric acid. Then the slurry was washed to remove all the salts. Finally the collagen fiber was extracted with acetic acid solution at a pH below 4.0, for one day under agitation and the amount of the acid was adjusted so as to obtain collagen solution of a concentration about 8%. After the extraction it was desirable to filter the solution in order to remove a small amount of non-collagenous materials remaining in the solution.

Then the collagen fiber slurry was neutralized, washed and extracted with acid as in Example 1.

The resulted collagen solution had the same properties as the product of Example 1 and could be converted to regenerated fiber and gelatin.

It was found that the molecular weight of the collagen in the solution was about 300,000; the molecule was 2800 Å in length, 15 Å in diameter, and had rigid rod like structure constructed of three polypeptide chains and was monomolecularly dissolved in the aqueous medium. When the collagen solution was spun through a nozzle into a coagulation bath according to a conventional process; the collagen was completely recovered as fiber.

When the collagen fiber slurry neutralized and washed, the collagen solution, or the regenerated collagen fiber dispersed in water was heated over the denaturation temperature of collagen, for example, to from about 50° to 60°C, the three polypeptide chains were separated into individual chains to form gelatin having a uniform molecular weight and an isoionic point of about pH 4.9.

Example 2

Steer bone was treated with 1.2 N hydrochloric acid for seven days during which the acid was replaced by fresh solution every day to obtain ossein containing a large amount of collagen. To obtain the insoluble collagen the ossein was treated, as in Example 1, but alkali-treatment was as follows:

collagen fiber	100	g
NaOH	20	g
Na ₂ SO ₄	100	g
dimethylamine	4.5	g
volume of solution	1	l
temperature	15	°C
duration	2	weeks

Example 3-6

Collagen fiber as in Example 1 was treated according to the procedures of Example 1, but alkali-treatment was as follows:

	Ex. 3	Ex. 4	Ex. 5	Ex. 6
liquid/fiber ratio	10	10	10	10
collagen fiber	100 g	100 g	100 g	100 g
NaOH	32 g	32 g	28 g	40 g
Na ₂ SO ₄	250 g	160 g	160 g	160 g
hydrazine (H ₂ N-NH ₂ ·H ₂ O)	15 g	—	—	—
ethylenediamine	—	12 g	—	—
hydroxylamine sulfate	—	—	16.4 g	—
piperazine	—	—	—	4.3 g
temperature	25°C	20°C	20°C	20°C
duration (week)	1	1	1	1

Example 7

The procedures of Example 2 were followed but alkali-treatment conditions were as follows:

liquid/fiber ratio	10
collagen fiber	100 g
NaOH	20 g
Na ₂ SO ₄	100 g
piperidine	17 g

5 The properties of the collagen solution obtained by Examples 3 to 7 were the same as those in Examples 1 and 2. The collagens could be converted to regenerated fiber and gelatin.

WHAT WE CLAIM IS:—

10 1. A process for dissolving insoluble collagen which comprises soaking insoluble collagen fiber in an aqueous solution containing alkali metal hydroxide, alkali metal sulfate and a small amount of base selected from hydroxylamine, hydrazine and primary or secondary, straight, branched or cyclic amines containing 1 to 5 carbon atoms, desalting the fiber slurry and treating the collagen fiber with acid solution having a pH below 4.

20 2. A process as claimed in claim 1 which further comprises converting the collagen solution into regenerated collagen articles.

25 3. A process as claimed in claim 1 which further comprises heating the resulting collagen solution at a temperature above the denaturation temperature of collagen to produce gelatin.

4. A process as claimed in claim 2 which further comprises heating the regenerated

fiber in water at a temperature above the denaturation temperature of collagen to produce gelatin.

30 5. A process as claimed in any preceding claim in which the concentration of alkali metal hydroxide is from 0.3 to 1.0 N.

6. A process as claimed in any preceding claim in which the concentration of alkali metal sulfate is from 10% to 20% (w/v).

35 7. A process as claimed in any preceding claim in which the concentration of base is from 0.05 to 0.3 M.

8. A process for dissolving insoluble collagen substantially as hereinbefore described with reference to the foregoing Examples.

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DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Gas-powder Contact Process and Apparatus therefor

We, MITSUBISHI JUKOGYO KABUSHIKI KAISHA, a Japanese Company, of 10, Marunouchi 2-chome, Chiyoda-ku Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention generally relates to gas-solid contact apparatus and procedures and is particularly directed to a method of and apparatus for establishing intimate contact between a particulate solid, such as powder, and a waste gas flow in which the particulate solid is distributed or dispersed, which waste gas flow includes sulfur oxides that are to be removed.

According to one aspect of the present invention there is provided a method for establishing intimate contact between a particulate solid and a flow of waste gas from which sulfur oxides are to be removed, which comprises dividing the gas flow into first and second portions, admixing particulate solid with said second portion, the particulate solid being capable of removing said sulfur oxides, combining thereafter said first and second portions of gas flow whereby a combined gas flow with particulate solid dispersed therein is obtained, and thereafter separating the dispersed particulate solid from the combined gas flow.

According to a further aspect of the present invention there is provided apparatus for mixing a gas flow with particulate solid, comprising in combination; first conduit means for conveying the gas flow, second conduit means for branching off a portion of the gas flow from said first conduit means, means for supplying particulate solid to said branched off portion of the gas flow for dispersing the particulate solid in the gas flow, third conduit means for conveying said branched off portion of the gas flow enriched

with particulate solid material back to said first conduit means, means for separating the particulate solid from the gas flow, contact means inter-positioned between said first conduit means and said separating means for causing intimate contact between the solid and gas, said separating means consisting of a first separating station for coarse particulate solid and a second separating station for fine particulate solid, said second separating station communicating with said first separating station to receive gas flow therefrom, regenerating means for regeneration of the fine particulate solid separated in said second separating station, and conduit means for conveying the regenerated particulate solid to said dispersing means and for conveying the coarse particulate solid separated in said first separating station to said dispersing means.

For a better understanding of the invention and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawing in which the single Figure is a diagram of one embodiment of apparatus for continuously removing sulfur oxides from a waste gas flow by means of particulate solids and for re-generating the solids after contact with the gas flow and recycling of the regenerated solid to the gas flow. The sulfur oxides are referred to hereinafter as "the contaminants".

Referring now to the drawing, the waste gas flow from which the contaminants are to be removed is indicated by the arrow 1' and enters the apparatus through main conduit 1. A part of the gas flow 1' is branched off through line 2 and flows through conduit 2' to enter a powder dispersing means 4. A blower 3 is connected between lines 2 and 2' to accelerate the flow of the gas into the dispersing means 4. Particulate solid, e.g. powder, is supplied to the dispersing means

[Price 4s. 6d.]

4 from a feeder means 20. An intimate mixture of gas and powder is thus formed in means 4 which is conveyed through conduit 5 back into the main stream 1' of the gas which flows through conduit 1. If the grain size of the powder is too large, suitable comminuting means may be provided at a suitable location in the system to enrich the gas flow with powder of suitable grain size. Conduit 10 is of a construction so as to accelerate the flow of the powder-enriched gas and thus may include a venturi nozzle or the like whereby the gas-solid mixture enters the main stream of the gas at high speed.

15 The combined gas flow 1' now enters the ascending section 6 of the gas-solid column. By bleeding off a portion of the main gas flow and enriching that portion with the solid particles, whereafter the mixture is re-introduced into the main stream, a uniform dispersion of the solid particles throughout the gas stream is effected. The gas-solid mixture after having passed through the ascending portion 6 flows through the descending section 7 of the column. Section 7 is of larger diameter than section 6. Due to the intimate contact between the powder particles and the gas, effective removal of the contaminants from the gas by the solid particles takes place by absorption or adsorption. The gas-solid mixture exits at the bottom of column 7 through line 8 and enters the separator 9 constituting the first separating stage. The separator may be of the centrifugal type and the major portion of the powder particles are separated therein from the gas stream. This major portion consists of relatively large-size particles. The gas exits from the top of the separator through conduit 10 and enters an electrostatically operated precipitator or dust collector 11 where residual particles of fine size are removed from the gas stream. The thus purified gas stream is then discharged to the atmosphere through a chimney or the like as indicated at 12.

45 A portion of the solid separated in separator 9 and the entire amount of solid separated in precipitator 11 are thereafter conveyed to regenerating equipment indicated by reference numeral 15. This is done by means of conduits or conveying means 14 and 13, respectively. Absorbed or adsorbed contaminants are removed in the regenerating equipment and the powder is regenerated and activated. The regenerating treatment chosen is also such that an increase in the grain size of the particles to a suitable size occurs. Suitable regeneration processes are known. For example, a wet process is known in which fine particles are agglomerated to form particles of larger size, the process using a cohesive aqueous solution and the resultant particles being dried. As regards dry processes, pelletizers for this purpose are known.

65 A relatively large amount of solid particles

is added to the branch flow in the dispersing means 4 so as to maintain the solid to gas ratio at a high value. In fact, the amount of solid dispersed within the gas flow is usually several times to several tens of times as large as the equivalent amount of contaminants which are to be removed from the gas. This means that only a portion of the solid particles reacts with the contaminants while the major portion of the particles passes through the system without absorbing or adsorbing any contaminants. Therefore, only that minor portion of separated solid has to be regenerated which, in fact, has absorbed or adsorbed contaminants, the major portion of separated solid being directly recycled.

The reactivated, regenerated solid is conveyed from the regenerating equipment 15 through line 16 into a mixer 18. As previously mentioned, the regenerated solid material is again of suitable particle size, to wit, the fine grained fraction of the material fed to the regenerating equipment is enlarged as to its size by the regenerating treatment. The main portion of the material separated in the separator 9 is also fed to the mixer 18 through line 17 and it will be noted that this portion of the solid material reaches the mixer without any regeneration step being necessary. The material entering mixer 18 is mixed and then conveyed through line 19 to the feeding means 20 previously described. The operation may be effected continuously to render it more economical and to facilitate the gas purification treatment.

The dashed lines in the figure which apply to the feeding of the solid material indicate conventional conveyors or the like transporting means for the transfer of powder from one station to another.

The feeding means 20, the dispersing means 4 and the mixer 18 may all be of conventional construction and may be chosen in dependence on the desired properties and the characteristics and particle size of the respective solids.

The electrostatic precipitating means or dust collector 11 may be replaced by a filter-type separator, if desired.

The reactivated solid particles conveyed through line 16 and the major portion of the solid which is discharged from the centrifugal separator 9 through line 17 may be supplied to the branch flow flowing through line 2' into the dispersing means 4 through separate conduits, in which event the mixer 18 would be dispensed with and the separated solid quantities would then be directly fed into the dispersing means 4.

It should also be appreciated that the invention is not limited to the particular type of column shown in the drawing, but horizontally arranged columns or ducts can be used as well in the same manner.

The operation and principal features of the present invention are further explained as follows:

1. By dispensing a large amount of solid particles through the gas flow, the desired high ratio of solid to gas may be readily obtained. As previously set forth, the amount of solid may be in excess of the amount required to remove the contaminants and, in fact, may be at least ten times this amount. Due to the particular dispersing method, as used in accordance with this invention, uniform dispersion of such large amounts of solid is still obtained.

15 As set forth hereinabove, a high solid to gas ratio is employed and this would result in an increased load on the separating means 11. However, in accordance with the procedure of this invention, the load on the separating means 11 is decreased for the gas-solid mixture, after having passed through the column 6, 7, first enters the centrifugal type separator 9. The greater portion of the solid particles is separated in this separator and the major portion of this separated material is directly fed to the mixer 18 through conduit 17 for recycling to the gas flow. This means that the greater portion of the solid is directly recycled. Since the material which is separated in the separator 9 is of the same particle size as the material originally admixed with the gas flow in the dispersing means 4, no further steps have to be taken in order to enlarge the particle size of the material separated in the centrifugal separator. The collection efficiency of the centrifugal separator 9 is high and this reduces the load on the dispersing means. The reason for this is as follows. Since that portion of the solid which is of finer particle size is separated and collected in the electrostatic dust collector or precipitator 11, and is thereafter subjected to a regeneration treatment which increases the particle size to a desired value, most of the particles thus regenerated and enlarged, will be separated in the centrifugal separator 9. This means that no significant proportion of fine particles accumulates in the recycled solid. Therefore, even if the solid to gas ratio is increased, the load on the dust collectors or separators is not increased and the proportion of solid passing through the gas outlets of the separators is maintained at substantially a constant value. Further, since a portion of the solids collected in the separators is, reactivated in the regenerating equipment before being again supplied to the gas flow through the dispersing means, the absorption or adsorption activity of the solid is maintained at a constant value. These factors have been confirmed by the following experiment:

Sulfur oxides, to wit, sulfur dioxide and sulfur trioxide contained in a heavy oil combustion boiler flue gas in about 0.1 percent

by volume proportion, were removed by treating the flue gas flow with active manganese oxide powder. The particle size of the powder did not exceed 100μ . The illustrated apparatus of was used for the experiment. The capacity of the apparatus was $3000\text{Nm}^3/\text{hr}$ and 90 percent of the sulfur oxides were removed with the mole ratio of the sulfur oxides to the active manganese oxide being 20. The centrifugal separator 9 was a multicyclone and the collection efficiency in the multicyclone for the active manganese powder was 83 percent in the first stage, 85 percent in the second stage, and 89 percent in the third stage. This clearly indicates the improved sieving effect attained by the invention.

2. Cost reduction for supplying the solid or powder and uniform dispersion of the solid in the gas stream are due to the dispersion of the solid in a part flow of the gas which is branched off from the main gas stream. Then, after this branch flow has been sufficiently accelerated, it is again combined with the main gas stream. The volume of gas to be branched off is dependent on the amount of solid to be admixed with the gas flow. By maintaining the amount of solid in the branched-off gas flow at a value less than one kilogram per one kilogram of gas flow, the dispersion and transfer of the solid in the gas stream can be readily and uniformly conducted. The velocity of the branched-off gas flow, after it has exited from the dispersing means 4, to wit, when the branched-off gas flows through the venturi nozzle or the like of conduit 5 should preferably be five meters per second higher than the end velocity of the solid to be dispersed.

The fact that the dispersion effect obtained in accordance with this invention is much superior to that obtained in prior art equipment is confirmed by the high absorption rate for the contaminant as obtained in accordance with this invention. In this connection, reference is had to the above-mentioned Example. In the Example, the solid to gas ratio was 20, calculated as mole ratio. The amount of the solid is, however, about 60 grams per one kilogram of gas, if the mole ratio is converted into weight ratio. This means that about $1/16$ of the total gas amount is branched off from the main gas stream and one kilogram of solid may be added to one kilogram of the gas in the divided flow. It follows from the above that the cost for the energy and equipment necessary for dispersing the solid in the gas in the above Example may be about $1/16$ of that required in conventional equipment wherein the solid is directly added to the entire volume of the gas. It will be appreciated, of course, that the amount of gas to be branched off from the main stream will depend on the particular contaminants and the nature of the gas

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flow to be treated. Generally speaking, however, it may be about one-tenth of the total volume of the gas to be treated.

It is generally very difficult uniformly to disperse solid particles in a gas stream. For example, in a large scale steam power plant in which the gas volume per power generator is 700,000 to 1,000,000 Nm³ per hour, the dispersion of a solid for removing contaminants from the waste gases is a major problem. It will be appreciated that this problem is significantly facilitated by dispersing the solid particles in a fraction of the flow only, for example in one-tenth of the entire gas volume and thereafter combining the branched gas flow with the main stream of the gas, in accordance with this invention.

In the embodiment shown in the figure of the drawing, the column is of the vertical type and the diameter of the descending section is larger than that of the ascending section. This construction has been chosen for the purpose of reducing the gas velocity and this is an effective means for increasing the retention time of the gas within the column while at the same time increasing the relative velocity of the gas and the solid. This, of course, in turn, results in an increased purification effect since the contact between the solid and the gas will be prolonged and more intimate.

However, it will be appreciated that the particular configuration of the flow passage through which the gas stream admixed with the solid is passed is not of critical importance for the purposes of this invention.

It will also be realized that the greater portion of the solid, to wit, a portion primarily consisting of coarser particles is separated and recovered in the first separating step by the centrifugal dust collector or separator, the remaining solid portion primarily consisting of fine particles which are recovered in the second step in the electrostatic precipitator. As previously mentioned, the electrostatic precipitator may be replaced by a filter-type dust collector.

Since the dispersion of the solids in the gas is effected in a dispersing means through which only a minor portion of the total amount of gas is passed, the size of the dispersing means may, of course, be considerably reduced as compared to prior art constructions. The reduction in pressure of the treated gas can also be greatly reduced in this manner as compared to procedures wherein the solid particles are directly dispersed in the main body of the gas flow.

WHAT WE CLAIM IS:—

1. A method for establishing intimate contact between a particulate solid and a flow of waste gas from which sulfur oxides are to be removed, which comprises dividing the gas flow into first and second portions, ad-

mixing particulate solid with said second portion, the particulate solid being capable of removing said sulfur oxides, combining thereafter said first and second portions of gas flow whereby a combined gas flow with particulate solid dispersed therein is obtained, and thereafter separating the dispersed particulate solid from the combined gas flow.

2. A method as claimed in claim 1, wherein the volume of said second portion of the gas flow is about one-tenth of the volume of the combined gas flow.

3. A method as claimed in claim 1, wherein said particulate solid is recycled to said second portion of the gas flow after it has been separated from the combined gas flow.

4. A method as claimed in claim 1, wherein said combined gas flow is passed through a contact zone prior to the separation of the particulate solid from the combined gas flow.

5. A method as claimed in claim 1, wherein the particulate solid is admixed with said second portion in an amount in excess of that required to remove the sulfur oxides from said combined gas flow whereby only a minor portion of the solid reacts with the sulfur oxides.

6. A method as claimed in claim 5, wherein the amount of said solid is at least ten times the amount required to remove the sulfur oxides from said combined gas flow.

7. A method as claimed in claim 1, wherein the particulate solid contained in said combined gas flow, prior to separation, comprises a mixture of relatively coarse particles and relatively fine particles, said separation being effected in two stages, to wit, a first stage in which said coarser particles are separated and a second stage in which said finer particles are separated.

8. A method as claimed in claim 7, wherein said separated particles of finer size and a portion of the particles of coarser size are regenerated, whereafter they are recycled, in conjunction with the remaining portion of said coarser particles to said second portion of the gas flow.

9. A method as claimed in claim 8, wherein the regeneration is carried out so as to obtain particles of said relatively coarse size.

10. A method as claimed in claim 7, wherein said first stage is carried out in a centrifugal separator.

11. A method as claimed in claim 7, wherein said second stage is carried out in an electrostatic precipitator.

12. A method as claimed in claim 7, wherein said second stage is carried out in a filter-type separator.

13. A method as claimed in claim 1, wherein said second portion of the gas flow is accelerated before it is combined with said first portion.

14. A method as claimed in claim 13, wherein the acceleration is such that the second portion has a velocity which is about 5 meters per second greater than the velocity of the combined flow. 30
- 5 15. A method as claimed in claim 1, wherein said gas flow is a waste gas containing sulfur oxides and said solid is manganese oxide powder. 35
- 10 16. Apparatus for mixing a gas flow with particulate solid, comprising in combination; first conduit means for conveying the gas flow, second conduit means for branching off a portion of the gas flow from said first conduit means, means for supplying particulate solid to said branched off portion of the gas flow for dispersing the particulate solid in the gas flow, third conduit means for conveying said branched off portion of the gas flow enriched with particulate solid material back to said first conduit means, means for separating the particulate solid from the gas flow, contact means interpositioned between said first conduit means and said separating means for causing intimate contact between the solid and gas, said separating means consisting of a first separating station for coarse particulate solid and a second separating station for fine particulate solid, said second separating station communicating with said first separating station to receive gas flow therefrom, regenerating means for regeneration of the fine particulate solid separated in said second separating station, and conduit means for conveying the regenerated particulate solid to said dispersing means and for conveying the coarse particulate solid separated in said first separating station to said dispersing means. 40
- 15 17. A method for establishing intimate contact between a particulate solid and a flow of waste gas substantially as described herein with reference to the accompanying drawing. 45
- 20 18. Apparatus for mixing a gas flow with particulate solid substantially as described herein with reference to the accompanying drawing.
- 25

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1119432

COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

